Impact of Phosphorus on NOx Aftertreatment Catalysts

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Objective

Compare the loss of NOx reduction performance over LNT and SCR catalysts due to phosphorus exposure using a laboratory diesel fuel burner

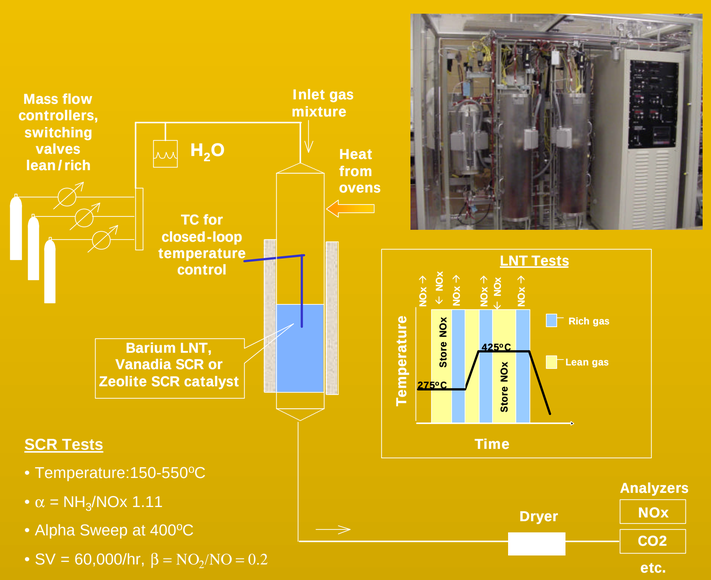
Characteristics of Phosphorus Deactivation

- **P source: Zinc Dialkyl Dithiophosphate (ZDDP) from Engine Oil**
- **P deposit distribution: More on catalyst inlet than on outlet**
- **Key factors: P concentration in the exhaust, not catalyst composition**

- **P deposit mechanism**
  - **Uncombusted ZDDP → $Zn_2P_2O_7$ amorphous glaze on catalyst**
  - **Combusted ZDDP → P_2O_5 (or H_2PO_4) which can react with catalyst**

- **Study focus: Impact of combusted ZDDP on catalyst performance**

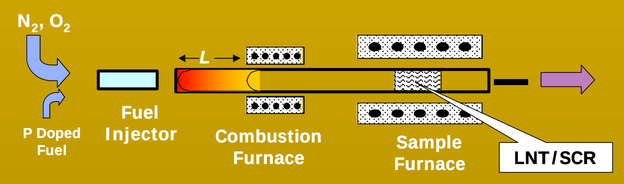
Catalyst Test Bench/Test Procedure



SCR Tests

- Temperature:150-550ºC
- α = NH_3/NOx 1.11
- Alpha Sweep at 400ºC
- SV = 60,000/hr, β = NO_2/NO = 0.2

Phosphorus Aging System

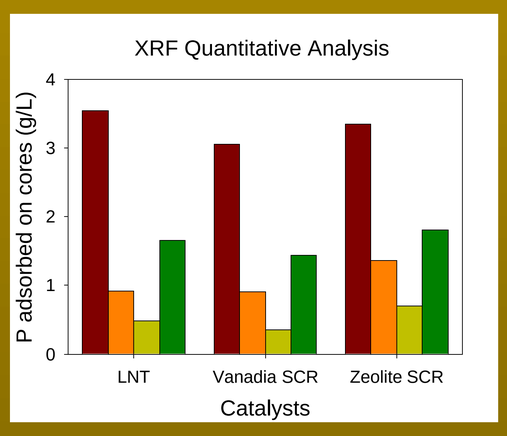


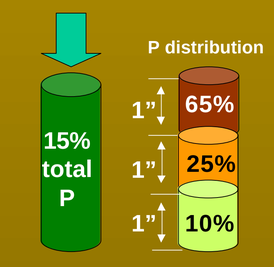
Phosphorus source: (TCP) Tricresyl Phosphate ($C_{21}H_{21}O_4P$) blended in zero sulfur diesel fuel

Exposure Time	Amount of P exposure/unit volume catalyst	Corresponding Time* on engine
90 minutes	3.6 (g/L)	4000 hrs
250 minutes	10 (g/L)	10000 hrs

***Assuming 800 ppm P in oil, 20L catalyst volume**

Phosphorus Deposition
(10 g/L Exposure)

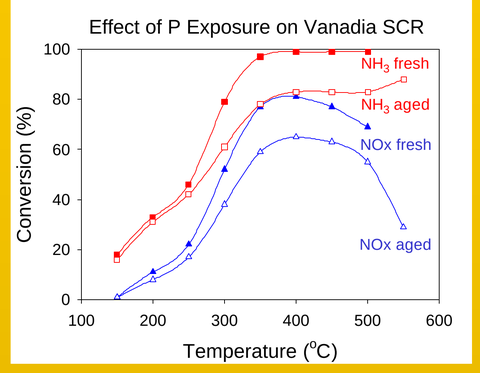




- **Similar amount of phosphorus adsorbed on each catalyst**
- **Non-selective deposition**

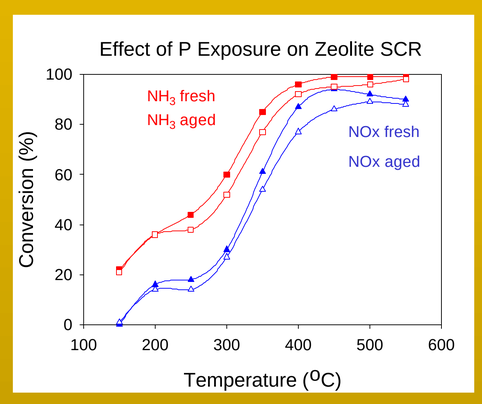
Results over Vanadia Catalyst

$$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O$$



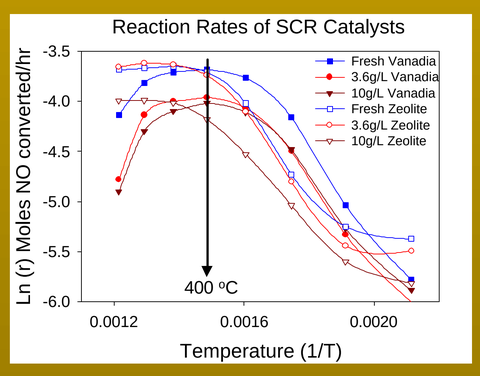
- **P impacts strongly at high temperature.**
- **P impacts both NOx and NH_3 conversions.**
- **Ammonia oxidation decreases NOx reduction.**

Results over Zeolite Catalyst



- **P impacts less on zeolite than vanadia catalyst.**
- **P impacts similarly in broad temp range.**
- **No drop off in activity at high temperature.**

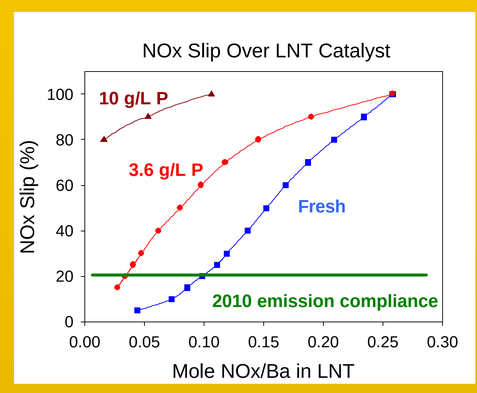
P Effect on SCR Kinetics



- **(< 400 ºC): Kinetic limited reaction, less P impact**
- **(> 400 ºC): Diffusion limited reaction, more P impact**
- **Similar kinetics for both vanadia and zeolite catalysts**
- **P capacity: zeolite > vanadia (due to higher zeolite surface area)**
- **Increasing a decreases activity with increasing P**
- **P exposure hinders ammonia conversion over SCR catalysts.**

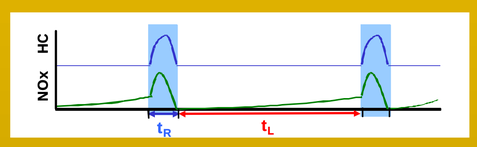
Results over LNT

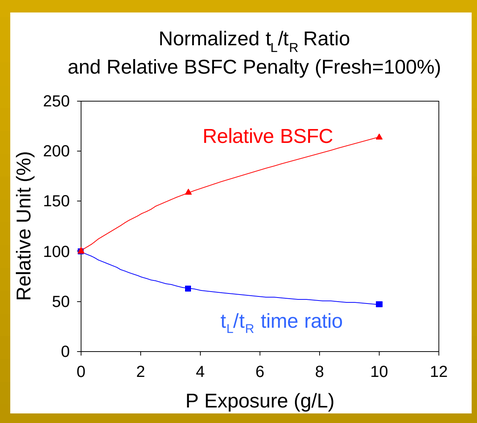
$NO + O_2 \xrightarrow{Pt} NO_2$	NO oxidation
$NO_2 + BaO \xrightarrow{Lean} BaNO_3$	Lean Storage
$BaNO_3 \xrightarrow{Rich,Rh} BaO + N_2 + O_2$	Rich Release + Reduction



- **Loss of NOx storage capacity with P exposure is the primary cause of decline in NOx conversions.**

Phosphorus Impact on LNT BSFC

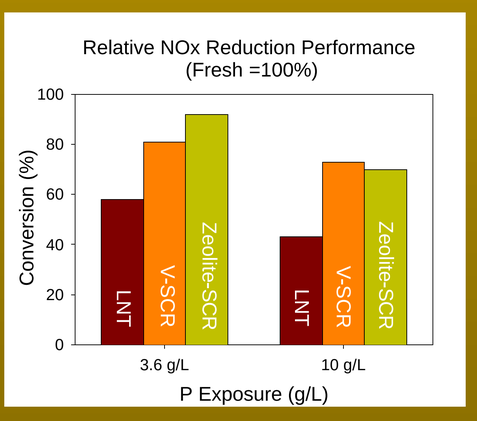




Assumptions

- **Constant amount of HC injection for rich pulse**
- **Constant t_R, variable t_L**
- **Increase # of rich pulses with decreasing NOx capacity**

Comparison of LNT vs. SCR



Summary

- **Over SCR catalysts**
  - **P similarly impacts both NH_3 and NO conversions.**
  - **Zeolite catalyst shows higher P tolerance initially, but both catalysts had similar deactivation after extended exposure.**
  - **P blocks NH_3 adsorption sites which prevent NO reduction.**
- **Over LNT catalysts**
  - **P impacts significantly on NOx storage capacity leading to decreased NO conversion.**
  - **P impacts more on NOx capacity at low NOx slip than at high slip.**
  - **P impacts less on NO oxidation function.**

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Conclusions

- **Phosphorus reduces NOx reduction catalyst performance and increases BSFC penalty.**
- **Phosphorus impacts LNTs more than SCRs but presents a challenge for both strategies.**

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